DESULFURIZATION OF THE CRUDE OIL USING ELECTRO-MEMBRANE FLOW REACTOR & FILM SHEAR REACTOR

Munzir Hamedelniel Mohamed Suliman

DEPARTMENT OF CHEMISTRY

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BY

Munzir Hamedelniel Mohamed Suliman

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This thesis, written by Munzir Hamedelniel Mohamed Suliman under the direction his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN CHEMISTRY.**

Dr. **Mohammed Nahid Siddique**
(Advisor)

31/12/2015

Dr. Abdulaziz Al-saadi
Department Chairman

Dr. **Basheer Chanbasha**
(Member)

Dr. Salam A. Zummo
Dean of Graduate Studies

Dr. **Abdulrahman Ahmed Al-Arfaj**
(Member)

5/1/16

Date

This work is to dedicated to my beloved family my mother, father, brother and sister

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LIST OF ABBREVIATIONS

HDS	:	HydroDeSulfurization
AgNPs	:	Silver NanoParticles
GC-SCD	:	Gas Chromatography-Sulfur Chemiluminescence Detector
Thio	:	Thiophene
BT	:	BenzoThiophene
mBT	:	methylBenzoThiophene
dmBT	:	dimethylBenzoThiophene
DBT	:	DiBenzoThiophene
mDBT	:	methylDiBenzoThiophene

ABSTRACT

Full Name : [Munzir Hamedelniel Mohamed Suliman]

Thesis Title : [Desulfurization of the Crude Oil Using Electro-Membrane Flow Reactor & Film Shear Reactor]

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The existence of sulfur compounds in the crude oil is one of the major problems for the pipelines and storage tanks and machines of petroleum refining. The trace amount of sulfur contaminants leads to corrosion and other problems like the emission of SO_2 which has a high impact on the environment. The removal of the sulfur compounds isn't an easy task, and achieving near-zero sulfur levels is technically challenging and highly costly. Many methods were reported for the removal of these compounds such as hydrodesulphurization (HDS), oxidative desulfurization, absorption and solvent assisted desulfurization but none of these methods is able to eliminate completely the sulfur contaminants. In this work the novel methods were used for the removal of sulfur contaminants from crude oil model (diesel), using silver nanoparticle coated membrane assisted flow and film shear reactor, these approaches are very simple, fast and very efficient for the removal of sulfur compound from the crude oil sample samples without any additional further pre-treatment, the both methods showed high sulfur compound removal up to 80%, and finally the film shear reactor was combined with membrane reactor and high removal for sulfur compounds was achieved.

ملخص الرسالة

الاسم الكامل: منذر حمد النيل محمد سليمان

عنوان الرسالة: ازلة مركبات الكبريت من البترول الخام باستخدام مفاعل الغشاء الكهربي و مفاعل الفلم القصي

التخصص: الكيمياء

تاريخ الدرجة العلمية: نوفمبر 2015

تواجد مركبات الكبريت في خام البترول يعتبر من اكبر المشاكل لانابيب, خزانات و ماكينات تكرير البترول, توجد مركبات الكبريت بنسب قليلة جدا يؤدي لمشاكل التأكل ومشاكل اخرى كانبعاثات غاز ثاني أوكسيد الكبريت الذي له تاثير كبير على البيئة.

ازالة هذه المركبات ليس بالمهمة السهلة والوصول الى تراكيز قريبة من الصفر يمثل تحدي تقني وذو تكلفة عالية. هنالك عدة طرق استخدمت لازالة هذه المركبات منها ازالة الكبريت الهيدروجينية, ازالة الكبريت بالاكسدة, بالادمصاص و الاستخلاص بالمذيبات وكل هذه الطرق ليست قادرة على ازاله المركبات تماما.

في هذا البحث استخدمت طرق فريدة في ازاله هذه المركبات, هي مفاعل الغشاء الكهربي المغلف بجسيمات الفضه النانوية و مفاعل الفلم القصي, هذه الطرق بسيطه, سريعة جدا و فاعلة وتصل نسبة ازالة مركبات الكبريت الي 80 % وفي النهاية تم دمج مفاعل الغشاء الكهربي مع مفاعل الفلم القصي وتم التحصل على نسبة ازاله عالية جدا.

CHAPTER 1
INTRODUCTION

1.1. Historical background

The removal of sulfur compounds from crude oil is very important to improve its quality. The sulfur compounds (such as thiophenes, benzothiophenes, dibenzothiophene and their derivatives) are naturally present in the crude. In recent years, deep desulfurization of diesel fuel has attracted much attention due to the gradual reduction of the statutory sulfur content in most western countries. In the near future the maximum sulfur content will be limited down to 10–50 ppm compared to today's value of 500 ppm. These efforts aim to limit SO_2 emission from diesel engines which has bad impacts on the environment like air pollution and acidic rain and other effects and also to protect equipment from corrosion [1].

In industry, desulfurization of diesel is actually carried out by hydro-treating. Generally, this allows the elimination of aliphatic and alicyclic sulfur compounds. However, if H_2S dissolved in the oil in the presence of air elemental sulfur is formed [2], and the removal of it difficult using distillation because the elemental sulfur change it structure with the temperature (from S_2, S_6, S_7, and then finally changes to S_8) [3] , many other methods reported for the desulfurization.

1.2. Statement of problem

The existence of sulfur compounds in the crude oil is causing challenging problems since long time because of their impacts on the environment and the oil containers. That's why ultra-low sulfur oil is highly required and all nation focus on produce oil with sulfur contain about 50 -100 ppm.

The removal of these compounds is very tedious task due to the low concentration of the sulfur compounds in the crude oil, and also because of the viscous matrix of the crude oil.

Due to these reasons we can see that why the hydro desulfurization method is very costly methods that require a high hydrogen gas pressure.

1.3. Aim of the study

The desulfurization is very important to produce oil and save the environment, that's why the companies evaluates the technologies to meet the requirement of the efficiency and the cost for the removal of these compounds from the fuel.

The aim of this study is to evaluate the removal efficiency of the sulfur compounds from the crude oil using simple and inexpensive methods which are electro-membrane flow reactor and flow shear reactor each of them individually and both of them combined.

1.4. Research objective

The objectives of this research are divided into four parts:-

- The first part is about optimization of the parameters of the removal of the trace levels of the sulfur contaminants in the crude oil samples using Flow reactor membrane assisted.
- The second part to optimize the conditions of Film-shear reactor for the sulfur compounds removal from crude oil model.
- The third part is study the kinetic of the removal for membrane flow reactor.
- The fourth part is the combination of the Film shear reactor and membrane reactor and investigate the sulfur compounds removal

CHAPETR 2

LITERATURE REVIEW

2.1. Methods of removing sulfur contaminants from crude oil

One of the first methods for removing the sulfur compounds is hydrodesulfurization (HDS), in this method the sulfur in the crude oil is converted to H_2S using hydrogen gas at high pressure and temperature with heterogeneous transition metal catalyst such as $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts [4], this method can occurred through two pathways hydrogenations and hydrogenolysis as it demonstrated in the below figure.

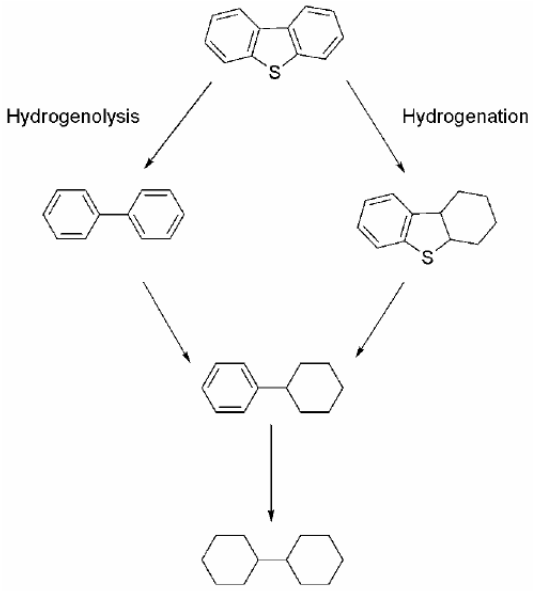
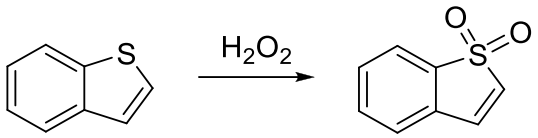


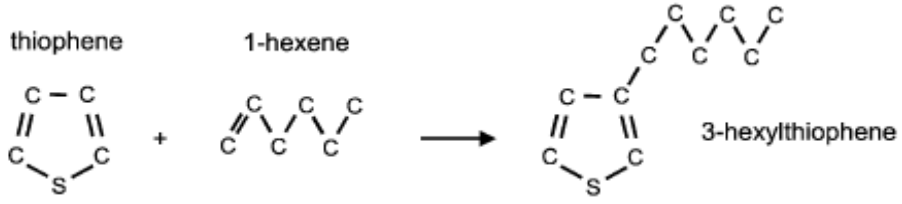
Figure 1: Mechanism of HDS

The hydro-desulfurization reduces the levels of sulfurs compounds considerably [5], however it has many disadvantages, this process is ran at high temperature, pressure, and log residence time that mean it consumes high energy and needs strong containers [6], also the HDS used for the removal of paraffinic compounds such as sulfides, disulfides, and thiols but some aromatic compounds resist the removal [7], another thing the hydrogen used in HDS reduces the olfienic compounds and that's reduces the calorific value of the crude oil, to solve this problem the product is sent to cracking catalyst and that consider additional cost [8].

A complementary alternative to HDS is oxidative desulfurization (ODS), most of sulfur contaminants that resist the hydrodesulfurization are reactive to the oxidative desulfurization condition, in this process an aqueous oxidant is used to react with sulfur and convert it into sulfoxides and sulfones, these sulfone show difference in the solubility which can easily be removed from the oil [9]. Many oxidant were used, peracids are the most commonly utilized oxidants, but a variety of inorganic oxidants have been used as well, including nitric acid, $NaBO_3 \bullet 4H_2O$, $Na_2Cr_2O_7$,/H+, $KMnO_4$, Ru on alumina, MoO_5/HMPA, and NaOCl/H+.[10-12] Additionally, catalysts such as $Sc(OTf)_3$, CH_3ReO_3, hydrotalcites, molybdenum, tungsten, and iron complexes have been used in conjunction with hydrogen peroxide as the oxidant to effectively convert sulfides and thiophenes to sulfoxides and sulfones.[13-17] Bicarbonate in combination with hydrogen peroxide has also been used, and even introduced as the anion of surfactants to promote aqueous phase activity of sulfides.[18]



Recently the nanomaterials were investigated in the oxidative desulfurization, Many other non-hydrosulfurization methods was used for sulfur compounds removal such as desulfurization by alkylation, this method based on the alkylation of sulfur compounds by their reaction with olefins using catalysts such as BF_3, $AlCl_3$, $ZnCl_2$, or $SbCl_5$ deposited on silica, alumina or silica–alumina supports [19]. These alkylated product have higher boiling point than the sulfur compounds and can be removed easily using distillation process [20].



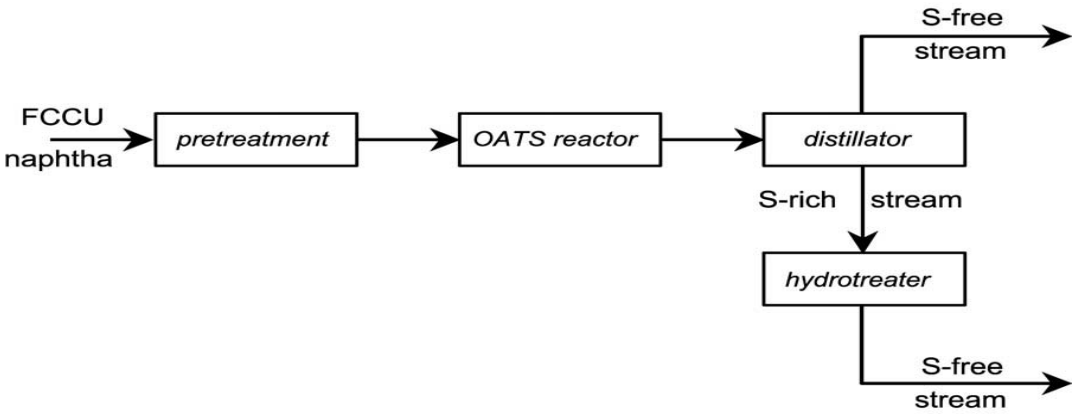
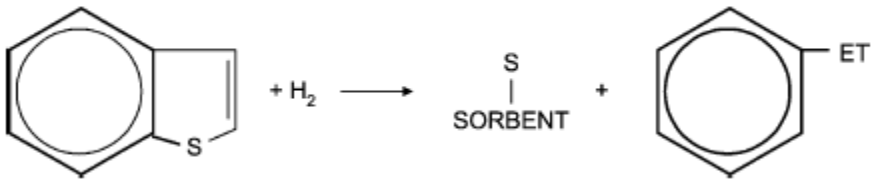


Figure 2: Alkylation desulfurization process

Other non-hydrosulfurization method was use which is the desulfurization by precipitation this process depend on the formation of insoluble complex, an example for this desulfurization was reported using 2,4,5,7-tetranitro-9-fluorene (TNF) as the most efficient π-acceptor as complexion agent[9]. But the removal percent was very low about 20% only also the selectivity of this reaction was weak because this reagent reacted with other compounds (non-sulfur compound) [21].

Adsorption solid sorbents also were used for the desulfurization, this process is depend on the ability of solid sorbent to adsorb the sulfur, the adsorption can be divided into two types, the first one is by the adsorption of the H_2S that generated from HDS process[22], the second type adsorb the sulfur contaminants directly and this is one is very likely because it takes place at ambient temperature and pressure[23], selectively this adsorption can be physical adsorption it's called adsorptive desulfurization in this case the sorbent can be generated easily, and when the adsorption is based on a chemical interaction it's called reactive adsorption desulfurization and in this case the regeneration of the sorbent

is more difficult than the first on because of the strong interaction and usually the sulfur binds as sulfide, many solid sorbent were used such activated carbon and zeolite [24,25].



Extraction methods were also applied for the removal of sulfur contaminants based on the solubility of sulfur in certain solvent is higher than the solubility of the hydrocarbon fraction, so the crude oil is mixed in a mixing tank with the solvent after that the mixture is transfer to a separator and the solvent (containing the sulfur) separated from the crude oil by distillation.

Different solvent were used such as ethanol, acetone [26] polyethylene glycols [27], and nitrogen containing solvents [28] showed a reasonable level of desulfurization of 50–90% sulfur removal, depending on the number of extraction cycles.

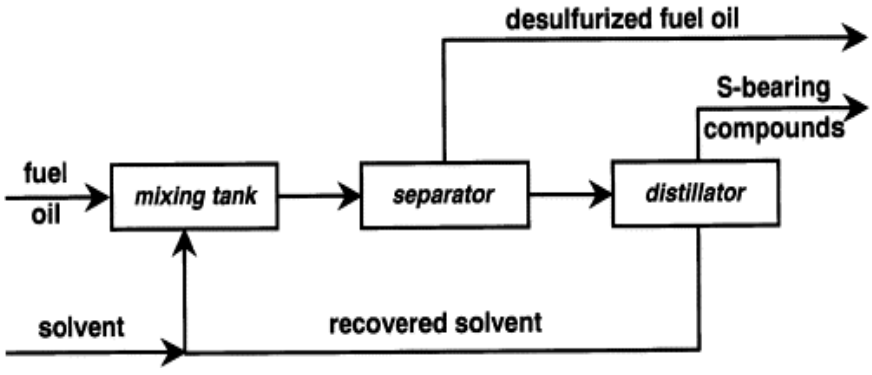


Figure 3: Extraction Desulfurization process

Many ionic liquids were used recently for the desulfurization of crude oil due to their unique properties such as negligible vapor pressure, high chemical and thermal stabilities, non-flammability, and recyclability. Example for ionic liquid used for this process 1-Butyl-3 methylimidazolium tetrachloroaluminate ([BMIM][$AlCl_4$]) and 1-octyl-3-methylimidazolium tetrafluoroborate ([OMIM][BF_4]).

This ionic liquid process was applied as a complementary process for the oxidative desulfurization by hydrogen peroxide and formic acid, and achieved high desulfurization efficiency about 95% [29].

Ionic liquid system	Percent sulfur removed
[BMIm]Cl/$AlCl_3$	45
[EMIm]Cl/$AlCl_3$	33
[$HN(C_6H_{11})Et_2$][CH_3SO_3]/ [$HNBu_3$][CH_3SO_3]	38

Table 1: Selected ionic liquied for desulfurizations

[30]

Another approach for fuel desulfurization is the bio-desulfurization, and that by use the microorganism to remove the sulfur, that's because sulfur is required to form the bacterial cell (more than 0.5% of the bacterial dry cell) sulfur is occurs in the structure of some enzymes like biotin, Co-enzyme A, and thiamine [31], some microorganisms can provide their needs of the required sulfur, and other type can consume the sulfur from the surrounding media, this type of desulfurization has its advantages, one of these advantages this desulfurization takes place at ambient temperature and pressure so it's energy saving method.

The bio-desulfurization are divided into three types, the first one called destructive bio-desulfurization, this one use the thiophenic compounds as carbon and sulfur sources [32-34], the second type of the bio-desulfurization is the anaerobic bio-desulfurization in this type anaerobic strain used to remove sulfur contaminants, and this strains have the ability to degrade about 96% and 42% of BT and DBT, respectively.[35], however it's not an easy task to maintain the condition for these strains for the desulfurization.[36], the third type called the specific oxidative desulfurization which can remove the sulfur specifically without the degradation of the hydrocarbon (non-destructively).[37]

2.2. Membrane extraction

Many organic compound were used for the direct removal of the sulfur compounds from crude oil such as formic acid, acetone and ethanol, but the removal efficiency by this method is very poor, that is due to simultaneous extraction of hydrocarbon [38], recently the membranes were used for the extraction of the samples with complex matrices, such as beverages, urine, soil, wastewater, and oil spills in the sediment samples[39,40], this method for removal is simple, efficient, and fast.[41]

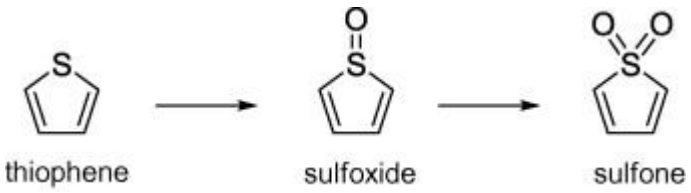
2.3. Electro-membrane extraction

Electro-membrane extraction is an extraction technique which the sample is extracted between donor and acceptor phase and using a potential as driving force [42], the first time this technique was used in 2006 to clean up ionic analyte from biological sample [43], this is method is fast, efficient, simple and green method because the small amount of the used solvent. [44], that why the EME was used in the pre-concentration of complex samples like: human plasma [45], whole blood [46] urine [47]. Saliva [48], breast milk [49], waste water [50], and tap mineral and river water [51]. In this work electro-membrane

extraction was applied, the role voltage is to enhance the removal of sulfur compounds, the negative electrode was placed in the sample and the positive electrode was dipped in the acceptor phase to attract the sulfur contaminants from the sample.

2.4. Film-shear reactor

A film-shear reactor is a device with a rotating disk, called a rotor, placed at an adjustable distance 20-300 μm from a stationary disk, called the stator, the rotor spins at speeds up to 10^4 rpm, and two solution streams containing the reactants are introduced between the two disks. The high speed of the rotor subjects the reactant solutions to exceptionally high shear rates (as high as 900,000 s^{-1} in our reactor), which mixes the solutions extraordinarily well so they react orders of magnitude faster than is possible in conventional reactors and micro-reactors, this reactor was used to enhance the oxidative desulfurization of thiophenes in fuels.



With selected conditions, one pass of a model fuel through the film-shear reactor provided up to 55% removal of benzothiophene in only seconds at temperatures as low as 10 C. Recirculation experiments showed that, if the flow rate and all other experimental parameters were held constant, the extent of thiophenes removal increased as the residence time increased. Experiments using various concentrations of hydrogen peroxide and different fuel oxidant ratios showed that, above a minimum amount, an increase in oxidant concentration did not lead to increased thiophene removal [52].

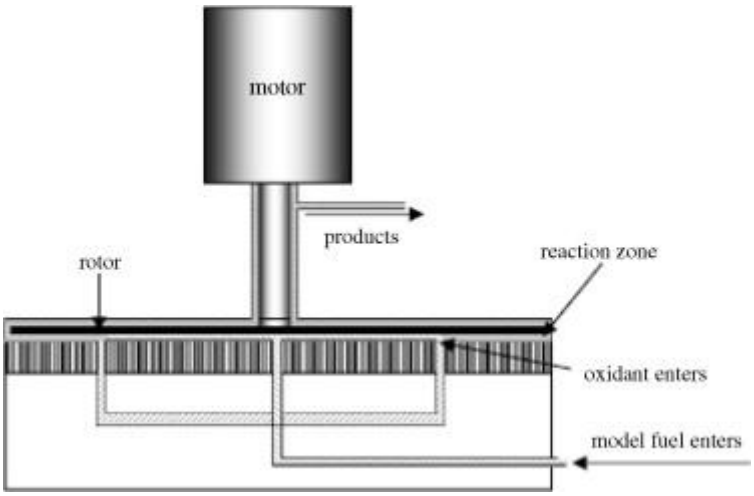


Figure 4: The Film shear reactor

CHAPTER 3

Experimental Section

3.1. Silver nanoparticle coated electro-membrane

3.1.1. Biosynthesis of Silver Nanoparticles

Basil (Ocimum basilicum) plant extract was used for the biosynthesis of silver nanoparticles. The plant extract was responsible for the reduction of $AgNO_3$ to silver nanoparticles and the subsequent capping and stabilizing of the synthesized nanoparticles [32]. 20g of the plant leaves were plucked, washed and boiled in 150 mL of deionized water. The plant extract solution formed is filtered using Whatmann filter paper and stored in the refrigerator at 4°C until further use. The plant extract was added to 2mM $AgNO_3$ in volume ratio 1:25 with the mixture adjusted to pH 8. After the addition of plant extract, the solution gradually turned from colorless to yellow and finally to dark brown. This confirms the existence of silver nanoparticles in the solution. The mixture was stirred for 2-hours at room temperature and subsequently centrifuged at 17, 000 rpm for 5 mins. The residue was collected and rinsed with ethanol. The nanoparticles obtained was further characterized.

3.1.2. AgNPs coated membrane

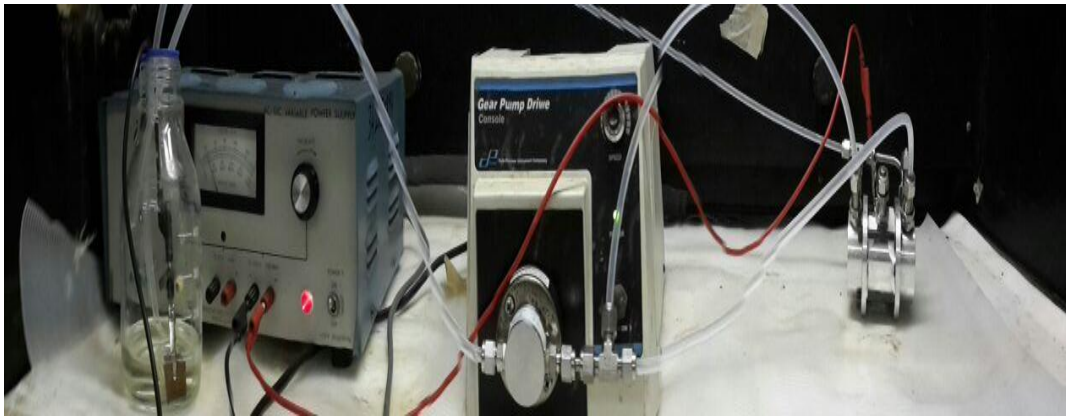
Two pieces of porous membrane (5x5 cm) were immersed in the AgNPs solution which was prepared above, after that the solution was placed in the shaker for 30^{o}C and sonication for 5 min, then after the membranes dried, they were placed in Flow reactor electro-membrane assisted.

3.1.3. Flow reactor electro-membrane assisted

The membrane flow reactor is consist of pump connected to the sample container (the donor phase) and to the reactor as it demonstrated in the below figure, the role of the pump is to flow the sample to the reactor and recirculate it for certain time and that increase the removal efficiency.

The reactor is consist of two zones the first on the two sides of the reactor for the donor phase and the second one in the middle for the acceptor phase solvent this solvent is used to extract the sulfur compounds from diesel sample (the donor phase), the two phases are separated by a porous membrane this membrane is act as a filter to allow the sulfur compounds to pass to the acceptor phase and exclude the hydrocarbon.

As it's clear in the figure there are two electrodes the negative electrode was inserted in the sample and the positive one in the acceptor phase, the role of the voltage is to enhance the removal of the sulfur compounds toward the acceptor phase by increasing the electrostaticity of the two phase, so the sulfur compounds have negative polarity so it will be attracted to the positive side the acceptor phase side.



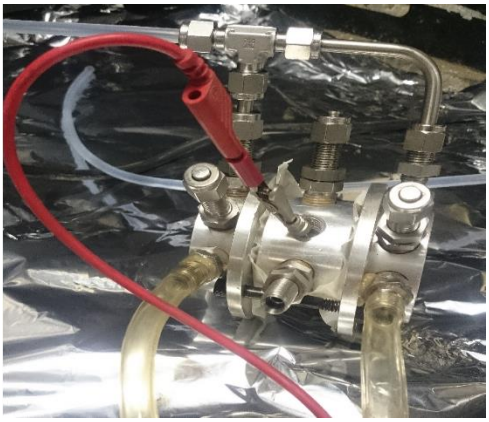


Figure 5: Represent A: flow reactor B: the reactor

A 100 ml of the diesel sample was placed in a beaker, and two pieces of porous membrane (5x5 cm) were placed in the reactor as demonstrated in the Figure 1. 5 ml of the acceptor phase was placed between the membranes, then the sample, the pump and the reactor were connected as shown in the figure and sample was circulated in the reactor for certain time and then the acceptor phase was transferred GC-SCD for analyses.

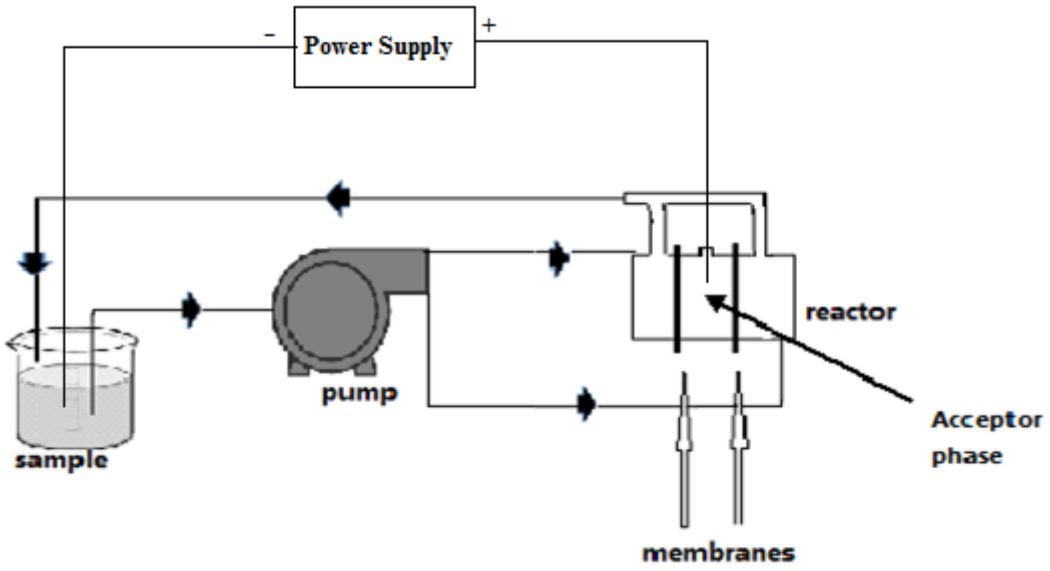


Figure 6: Electro-mediated flow reactor

Number of parameters such as membrane type, removal time, type of solvent used in acceptor phase, flow rate of the pump and the voltage were optimized using spiked diesel sample.

3.2. Film shear reactor

Film shear reactor is a device consist of two syringetic pumps each pump is connected to solutions and these pumps are connected to sycetron reactor, this reactor is a mixer

reactor with high speed rotating disk about 100,000 rpm and the adjustable distance between this rotor disk and the stator about few 100 μm, this high speed of the rotor disk and the small distance mix the two solutions as thin film so the mixing occur on the molecular level and that's gives a high removal efficiency in very short time (less than 1 minute) in compare with the other conventional reactors and batch methods.

There are some parameters to be optimized in this reactor such as the concentration of the solution pumped in the reactor, the speed of the reactor motor which is controlled by power supply, the combined flow rates for the two syringetic pumps, and the gap size between the rotor and stator adjusted by micrometer in the reactor.

Figure 7: Show the setup for a) Film shear reactor b) Synthetron reactor

3.2.1. Preparation of CNT/TiO_2 Composite

Carbon nanotubes were refluxed with (3:1) mixture of sulfuric acid and nitric acid with continuous heating at 120^{o}C for 8 hours, then the mixture was diluted and filtered, and to remove the excess acid the carbon nanotubes was washed by deionized water, after that the wet nanotubes was dried at 120 for overnight, then the nanotubes was crushed into powder, 0.1 g of the powder was dispersed by sonication for 4 hours, in another beaker viscous titania solution was prepared by hydrolyze 4.0g of titanium tetraisopropoxide solution, after that the solutions were mixed drop wise with continuous stirring, the solution was reflexed for 6 hours, filtered, and dried overnight, finally the dry product was calcinated at 350^{o}C for 3 hours, the composite was characterized using of field emission scanning electron microscope (FESEM), Energy dispersive X-ray spectroscopy (EDX) and Fourier transform infrared absorption spectroscopy (FTIR).

3.2.2. Model fuel solution

100 ppm solution of sulfur compounds (thiophene, benzothiophene, methylbenzothiophene, dimethylbenzothiophene, dibenzothiophene and methyldibenzothiophene) was prepared in diesel.

3.2.3. CNT-TiO2 Suspension solution preparation

0.01, 0.02, 0.05 and 0.1 wt/v % were prepared adding the nanocomposite to small amount of hexane then the solution was sonicated for 10 min after that the volume of the solution was completed to mark with hexane.

3.2.4. Film-shear reactor experimental

The first solution of the diesel was placed in the first pump, and the suspension of the nanocomposite was placed in the second pump with continuous stirring (to keep the suspension homogeneous), then the two solution were pumped into the reactor and the reactor was run, the parameters of the reactor (dosage, voltage, flow rate of the pump an the gap size) were optimized using the gas chromatography with sulfur chemiluminescence detector to evaluate the removal of sulfur compounds.

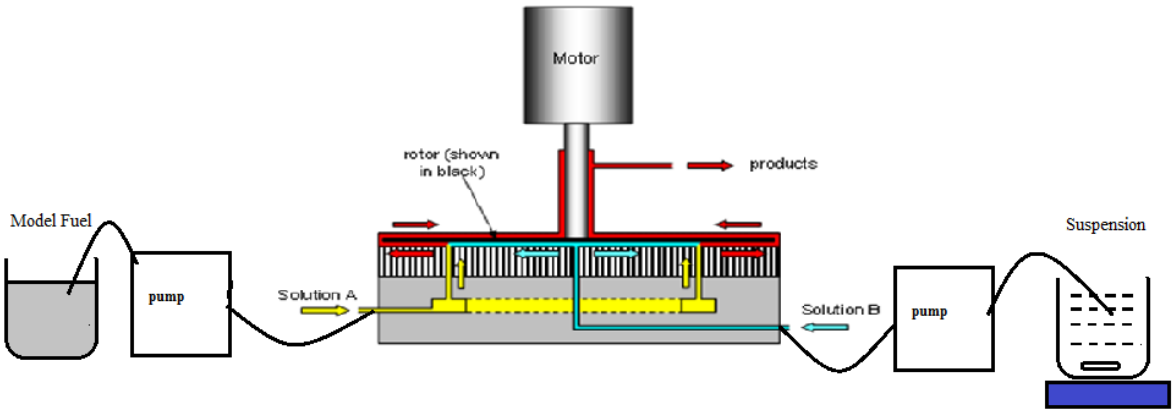


Figure 8: Film shear reactor experiment set

3.3. Combination of Film shear reactor and membrane reactor

The film shear reactor and membrane reactor were combined as it demonstrated in the figure below the optimum parameter for the both reactors were used after the sample flew in the membrane reactor it was passed in the film shear reactor and the sample was collected and injected in the GC-SCD to evaluate the removal.

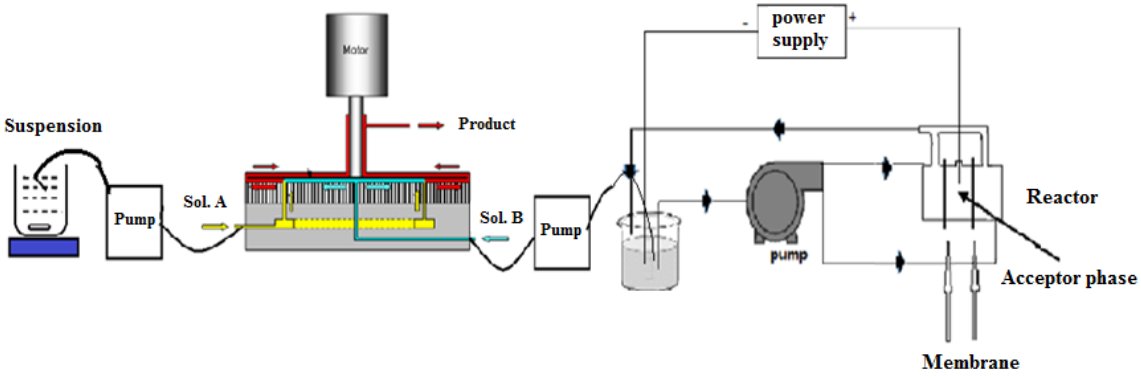


Figure 9: Combination of Film shear reactor and membrane reactor

3.4. GC/SCD:-

The instrument will be used in the experiment consist of GC system from Agilent technology 7890A with Autosampler 7683B series injector equipped with 10 µl syringe. HP – 1 fused silica column from Agilent technology (30m x 0.32 mm – 1 µm film – (-60 – 325^{o} C)) will be used for the separation of triphenylphosphine sulfide. The GC/SCD conditions will be optimized as the inlet temperature was as 250^{o}C, and the sample injection volume is 1 µl, carrier gas used is Helium and its flow rate is 3 mL/min. the GC oven temperature will be programmed at 250^{o} C

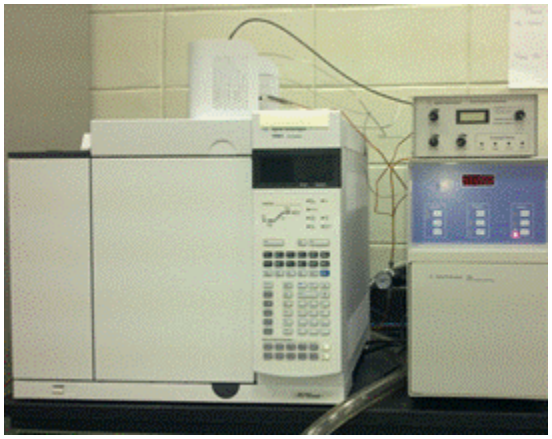


Figure 10: Gas Chromatography Sulfur Chemiluminescence Detector

CHAPTER 4

Results and Discussions

4.1. Silver nanoparticle coated electro-membrane

4.1.1. Characterization of AgNPs

The figure below is showing SEM images of AgNPs. SEM provided further insight into the morphology and size details of the biosynthesized AgNPs. The image shows that AgNPs are Colloids consist mainly of small nanoparticles having nearly spherical shape particles of size 7– 10 nm.

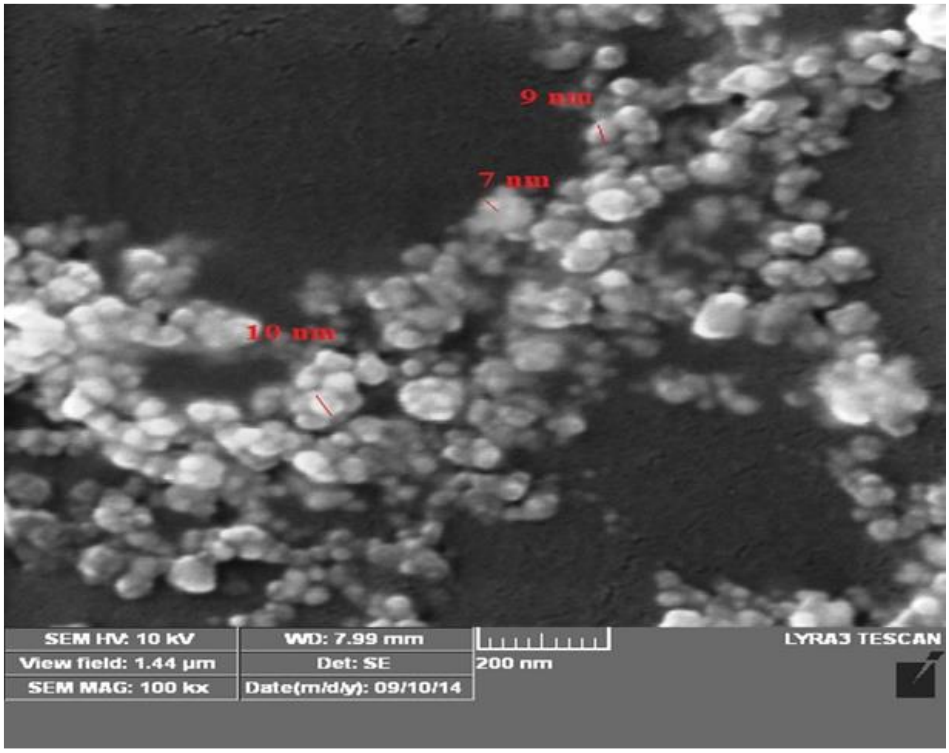


Figure 11: SEM image of the biosynthesized AgNPs

4.1.2. Characterization of biosynthesized AgNPs coated membrane

The figure below shows the SEM images of the coated and uncoated membrane with biosynthesized AgNPs. The first image shows our pure membrane, where the second image reveals the successful dispersion of AgNPs within the hollow fiber.

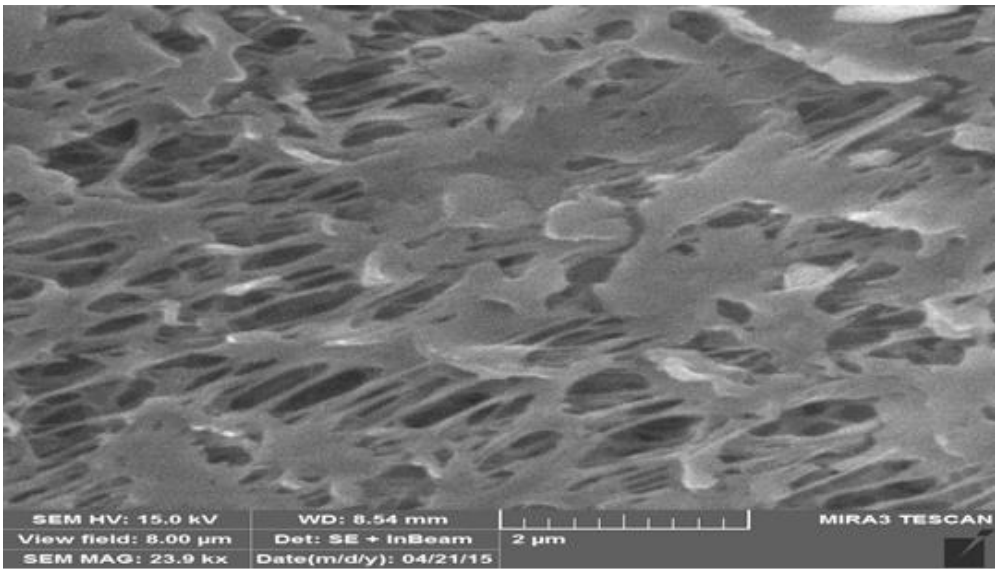


Figure 12: SEM images of uncoated membrane

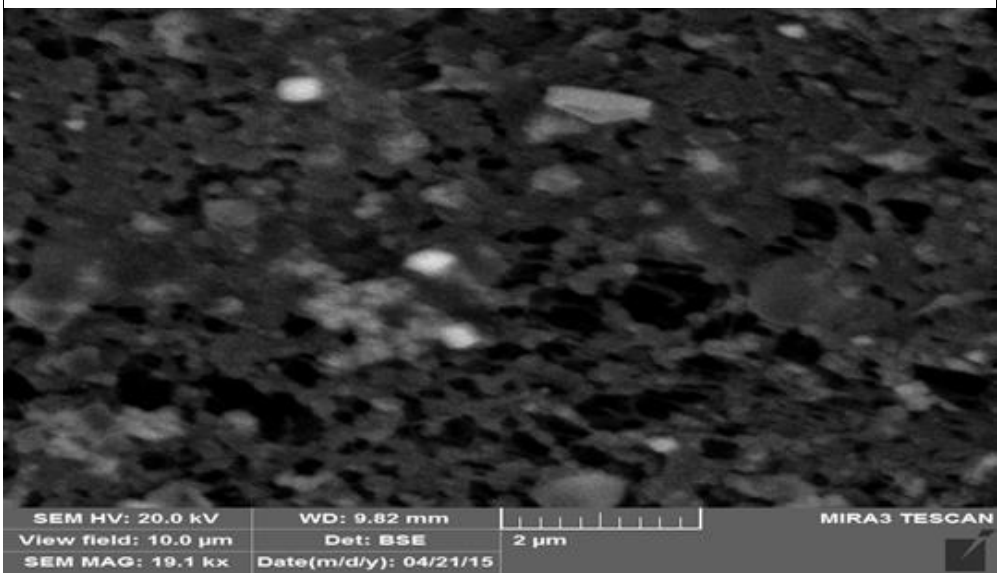


Figure 13: SEM images of biosynthesized AgNPs coated membrane

4.1.3 Desulfurization using membrane flow reactor

Many parameter were optimized for the membrane flow reactor: optimum membrane of the removal, the solvent for the removal, removal time, optimum flow rate for the pump used in the reactor and the voltage, the removal efficiency was evaluated using GC-SCD.

4.1.3.1 Optimization of the membrane and the solvent of the removal

The optimum membrane was investigated two different membranes were used (polypropylene and polysulfone membrane) and the optimum solvent also was investigated four different solvents were checked (acetone, toluene, hexane and acetonitrile), the criteria of selecting acceptor solvents is to select solvent which the sulfur compounds have higher solubility in that solvent than the fuel oil.

According to the figure (13) it's observed that the polysulfone membrane showed better removal efficiency than polypropylene membrane and for the removal solvents acetonitrile showed the best removal between the other solvents as it was reported nitrogen containing solvents are the most suitable solvent for sulfur compounds extraction.

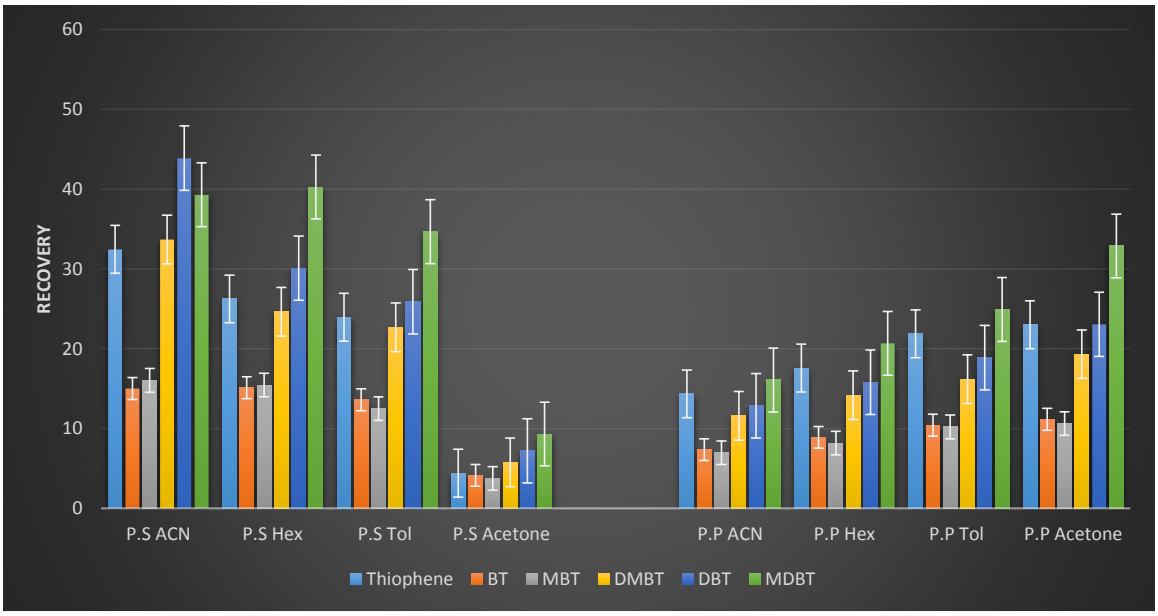


Figure 14: Optimization of membrane and solvent of removal

4.1.3.2 Optimization of the removal time

The optimum time of removal was investigated (from 10 to 50 min), different samples at different times (each 10 min) were tested using GC-SCD using polysulfone as membrane and acetonitrile as extraction solvent at 50 ml/min for the pump flow rate, and it was observed that from figure (14) the removal percent was increasing with the time until 40 min, after that there was no significant increase so 40 min was assigned as the optimum removal time.

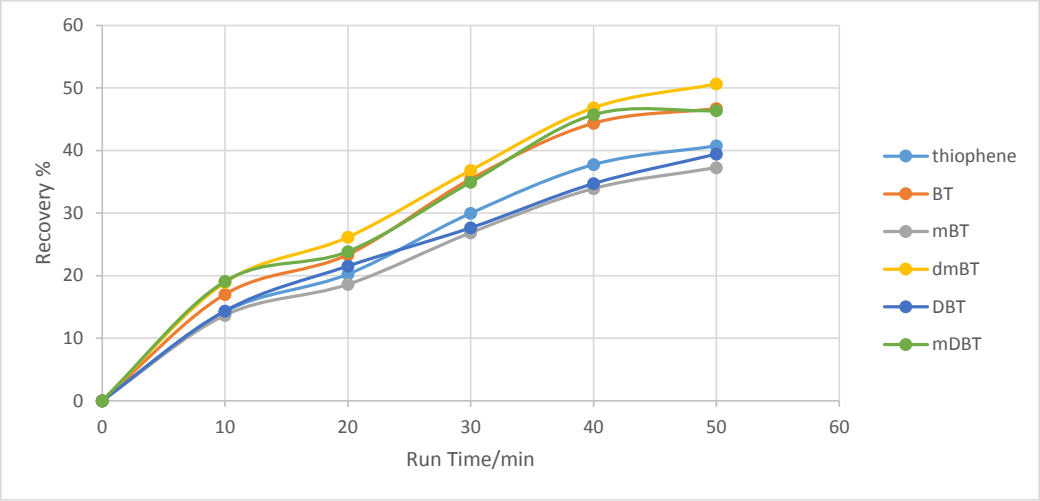


Figure 15: Optimization of removal time

4.1.3.3 Optimization of the flow rate of the pump

The flow rate of the pump was also optimized different samples were investigated at different flow rates for the pump using GC-SCD using polysulfone as membrane and acetonitrile as extraction solvent for 40 min, and it was clearly seen that from figure (15) 60 ml/min was the optimum flow rate.

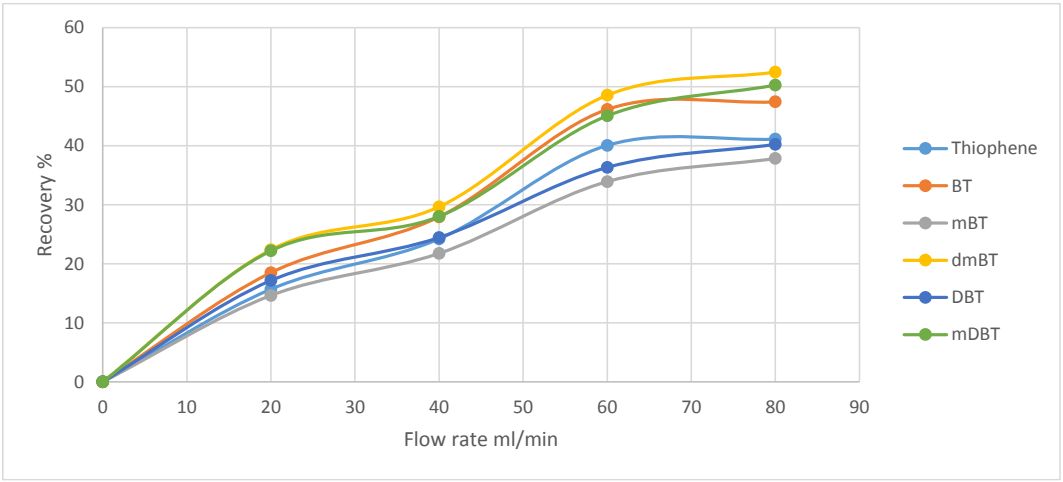


Figure 16: Optimization of pump flow rate

4.1.3.4 Optimization of the Voltage

The voltage also was optimized different voltage were used between 5 to 200 v using GC-SCD and using polysulfone as membrane and acetonitrile as extraction solvent at 60 ml/min for the pump flow rate for 40min and there was obvious enhancement in the sulfur compounds removal the optimum voltage 100 v as it can be seen clearly in the below figure, that because increasing the voltage increase the polarity of the acceptor phase, so the negatively polar sulfur compounds will be attracted to the positive polar acceptor phase.

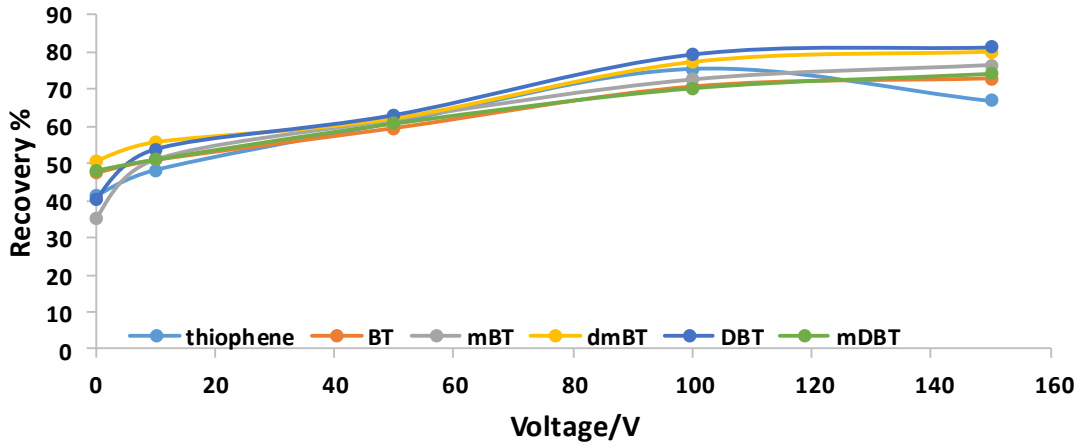


Figure 17: Optimization of the Voltage

4.1.4 Kinetics Studies

The kinetic studies show the relation between the acceptor phase and the donor phase, and can explain the mechanism of the removal, two models were applied to study the removal of sulfur compounds, first model is pseudo first order, and the second model is pseudo second order, the agreement between the experimental values and the models are indicated by correlation coefficient (R^2), higher value of (R^2) means the model describes

the removal, the kinetic of the removal was investigated by measuring the removal with the time and pseudo first order model and pseudo second order model were applied.

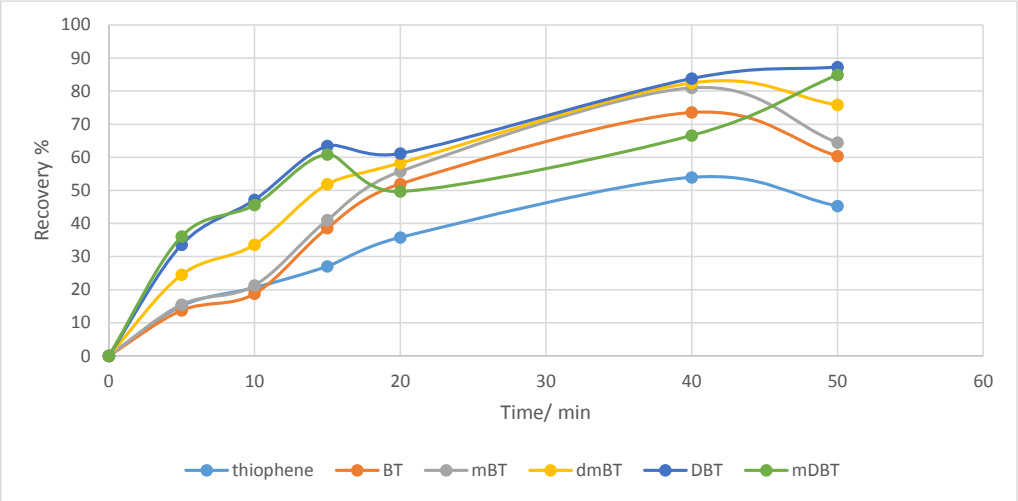


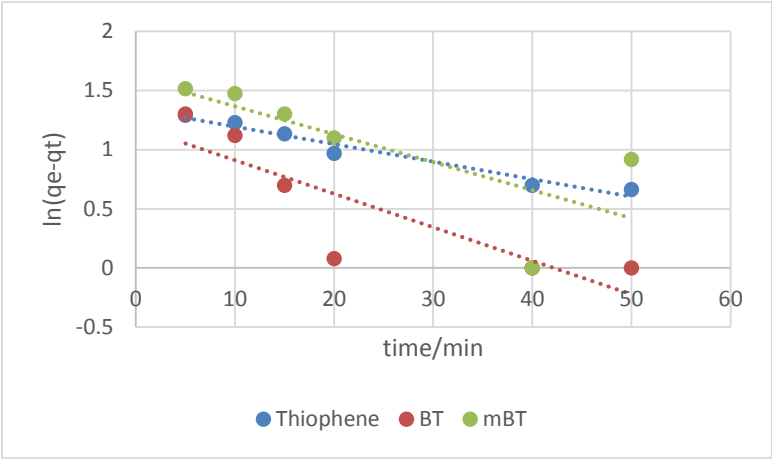
Figure 18: The study of the removal kinetic

4.1.4.1 Pseudo first order model

Pseudo first order model is expressed by the equation

$$\log(q_e - q_t) = \frac{\log q_e - k_1 t}{2.303} \qquad q_e = \frac{(C_0 - C_e)V}{W} \qquad q_t = \frac{(C_0 - C_t)V}{W}$$

This model indicate that the removal depend on one of the two phases, the donor phase or the acceptor phase, and by applying this model (log(qe-qt) against the time) the below graphs were obtained.



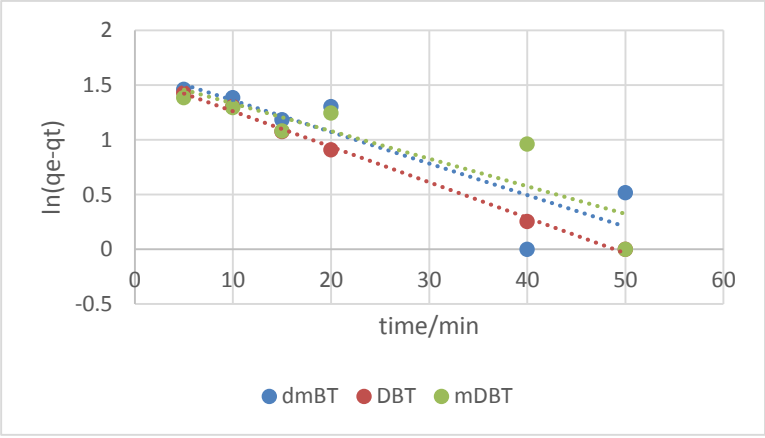


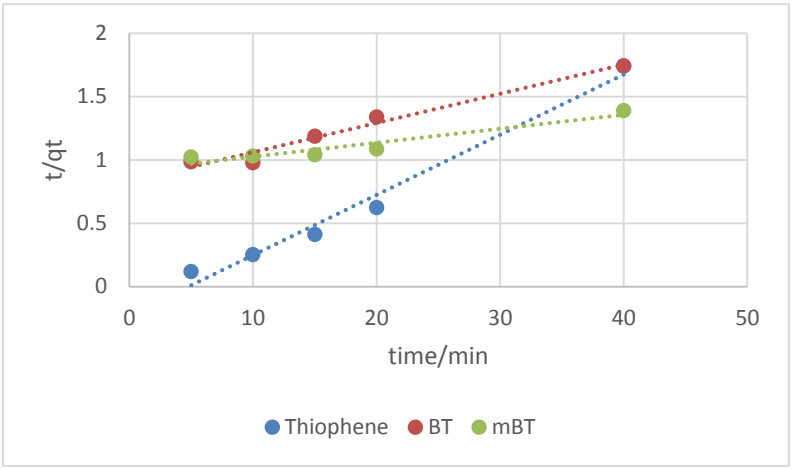
Figure 19: Pseudo first order model

4.1.4.2 Pseudo second order model

Pseudo second order model is expressed by the equation

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t}$$

This model is indicate that the removal depend on the both acceptor and donor phases, and by applying this model (by representing t/qt against the time) the below figures were obtained.



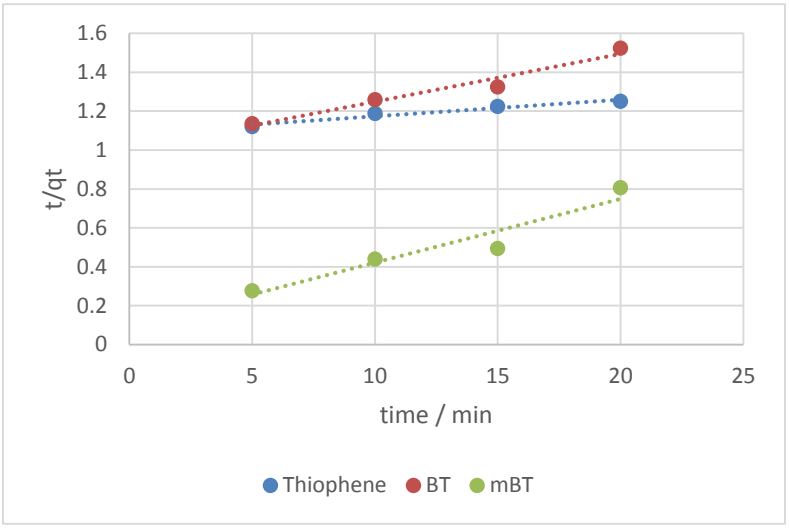


Figure 20: Pseudo second order model

	Pseudo first order					
	Thiophene	**BT**	**mBT**	**dmBT**	**DBT**	**mDBT**
R^2	0.7325	0.9671	0.7673	0.7325	0.9974	0.7469
	Pseudo second order					
	Thiophene	**BT**	**mBT**	**dmBT**	**DBT**	**mDBT**
R^2	0.9749	1.0000	0.9201	0.9782	0.9389	0.9664

Table 2: Summary of corrlation coefficients for the models

From the figures and the correlation coefficients summarized above it's clearly that the correlation coefficients for the pseudo first order model are relatively low so the removal kinetics fails to obey the pseudo first order model, and as we can see in the table the correlation coefficients for the pseudo second order are relatively high so the removal kinetics are fitted to the pseudo second order model.

4.2. Film shear reactor

4.2.1. Composite Characterization

4.2.1.1. X-ray Diffraction Spectroscopy

The structure of nanocomposite was characterized by XRD shown in the below figure. The XRD pattern of the CNT/TiO_2 nanomaterials confirms the presence of titania of anatase CNTs and the anatase TiO_2 peak (101) at the reflection plane of $2\theta = 25.3°$.

The peaks in the XRD pattern at 37.80 (004) 48.18 (200), and 54.09 (105) clearly represent the anatase TiO_2 phase.

From the XRD pattern, it can be understood that the anatase constitutes the major crystal form in CNT/TiO_2 composite

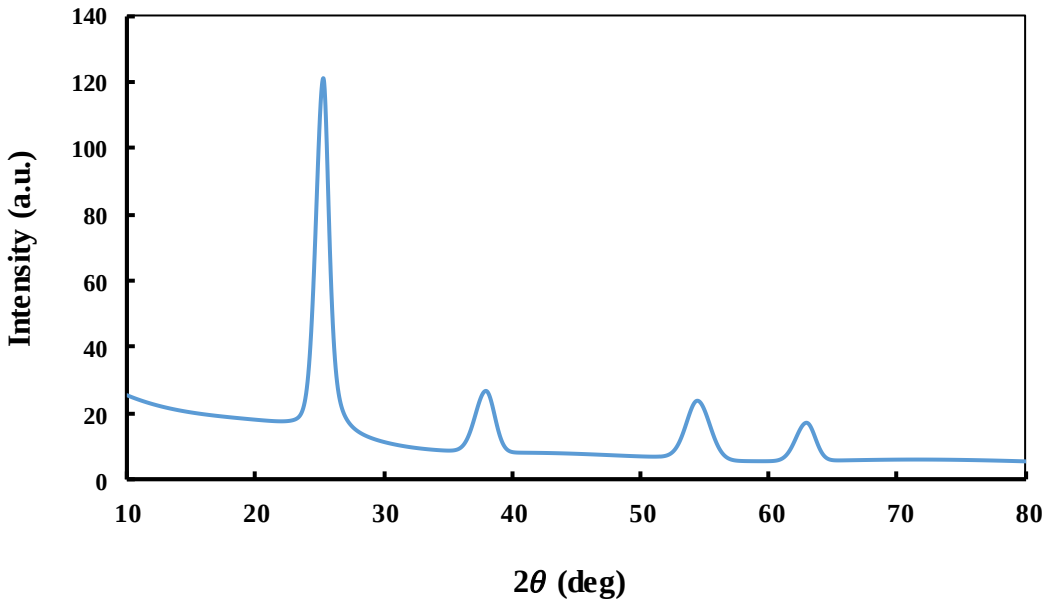
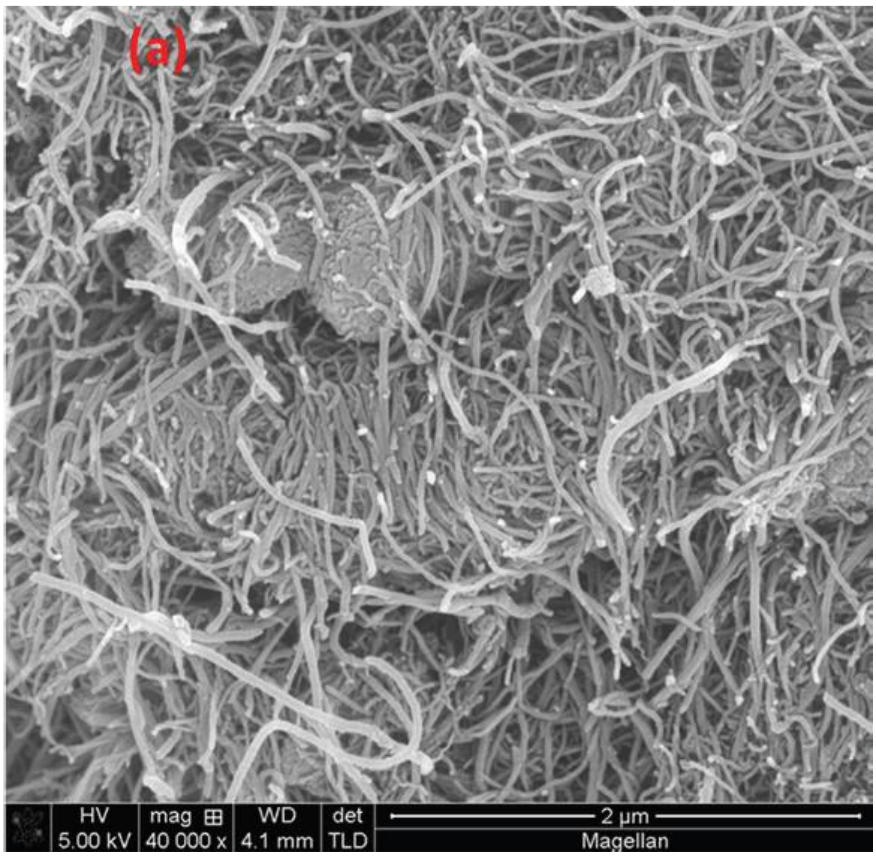


Figure 21: XRD of the MWCNT/TiO2 nanomaterials.

4.2.1.2. Field emission scanning electron microscope

The morphology of the prepared composite was characterized using field emission scanning electron microscope (FESEM), The SEM image is depicted in Figure belowand enlarge part of SEM image is depicted in Figure2 2b. The surface morphology of TiO_2 nanoparticles is ball like round shape or spherical shape decorated on the nanotubes. Based on these findings, one can induce that the nanocomposite has been successfully obtained and titania nanoparticles were deposited on the surface of the nanotubes.



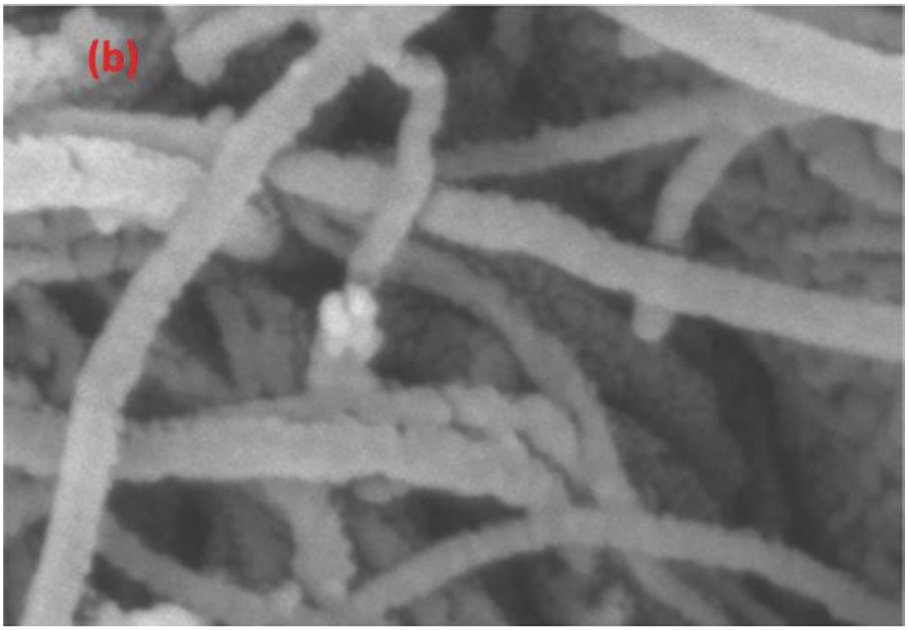


Figure 22: High resolution field emission scanning electron microscopy (FESEM) image (and enlarged SEM image of the MWCNT/TiO_2)

4.2.1.3. Energy dispersive X-ray spectroscopy

The Energy dispersive X-ray spectroscopy experiment was carried out and as we can see in the below figure the presence of titanium, oxygen and carbon elements that's formed the composite.

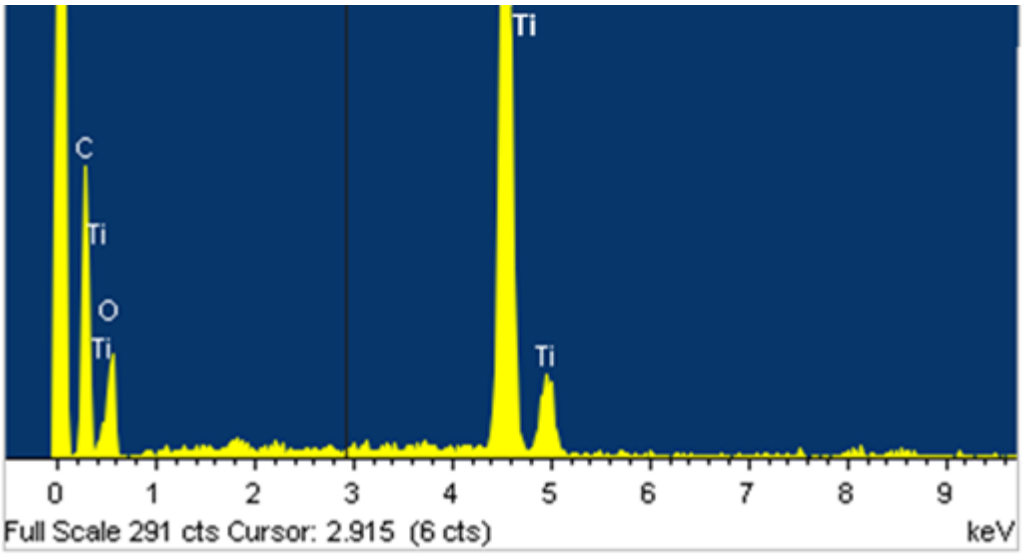


Figure 23: EDX spectrum of the MWCNT/TiO_2 nanomaterials.

4.2.1.4. Fourier transform infrared absorption spectroscopy

The Fourier transform infrared absorption spectroscopy showed the following peaks as it's clear in the FTIR spectrum, 1580 and 1650 cm^{-1} are characteristic for C=C and C=O on the CNT stretching vibration respectively, 1100 and 1400 cm^{-1} peaks are due to C-O stretching vibration and the Ti-O characteristic peak between 600-700 cm^{-1}

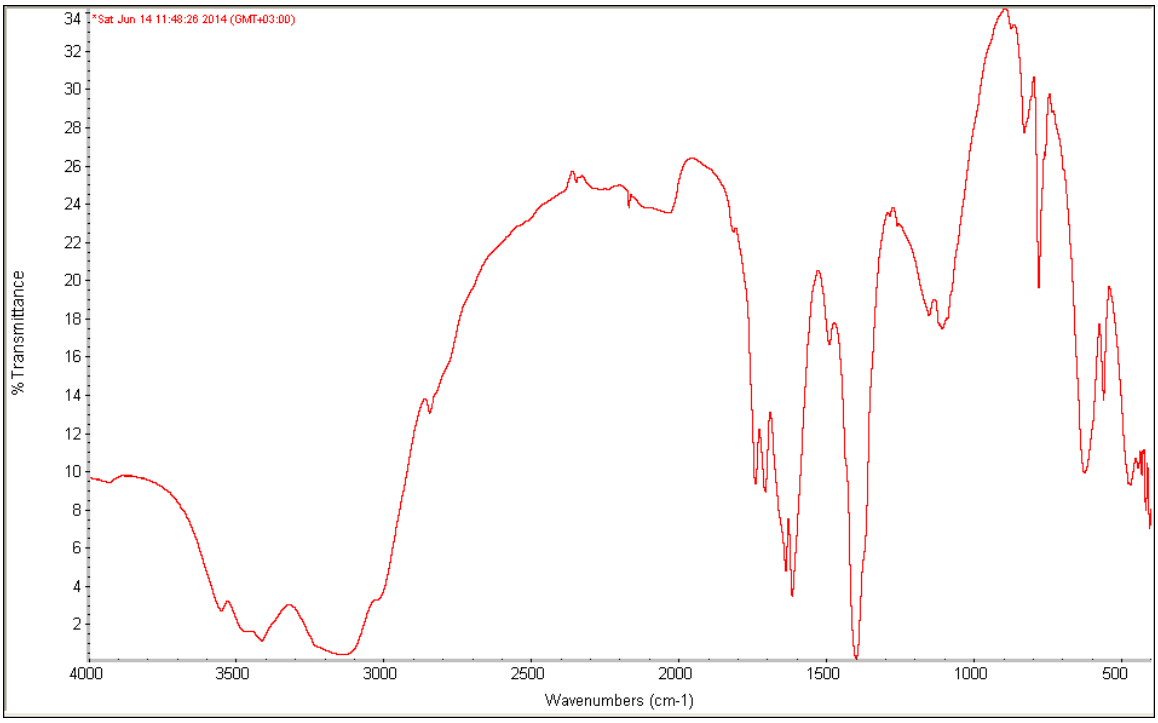


Figure 24: FTIR spectrum of the MWCNT/TiO_2 nanomaterials.

4.2.2. Optimization of the Parameters

Different parameters of the reactor were optimized such as the concentration of the sorbent, the speed of the motor, the combined flow rate of the two pump and the gap size of the film (reaction chamber).

4.2.1.1 Sorbent concentration:-

Different four concentrations of the suspension were used 0.01, 0.02, 0.05 and 0.1 wt/v%, and from the graph the removal was increasing with the increasing of concentration of nanocomposite suspension until 0.05% after there no change in the removal percent.

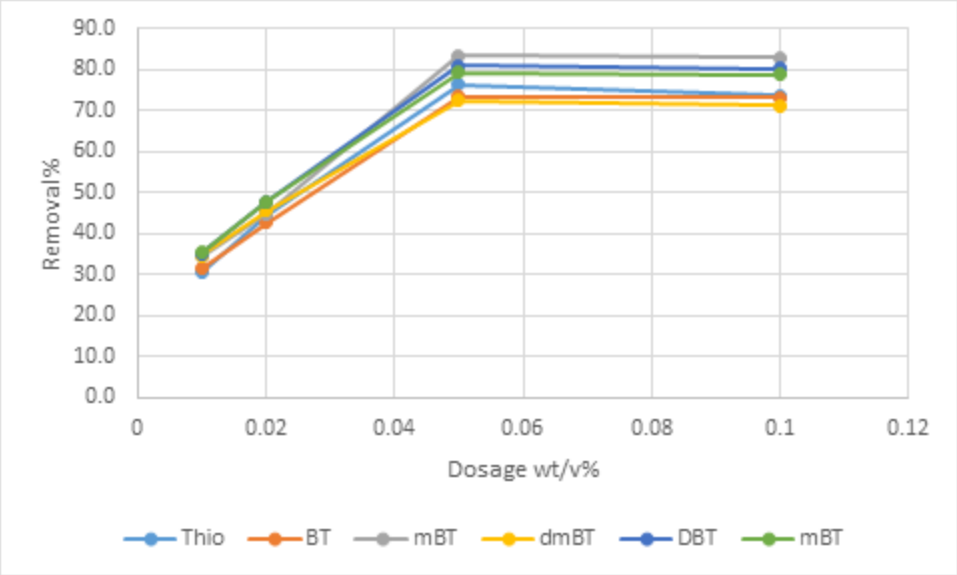


Figure 25: Optimization of sorbent concentration

4.2.1.2 Speed of the motor

The speed of the motor of the reactor was investigated by increasing the voltage the speed of motor in the reactor increase, four different voltages were investigated 3, 6, 9 and 12, using 10ml/min as pump flow rate and 100 µm for the reactor gap size from the graph by increasing the speed of the motor the removal efficiency increases that because increasing the motor speed increases the mixing rate and that increase the adsorption rate and removal efficiency until 9V which the speed of the motor in that voltage is equal to about 37000 rpm.

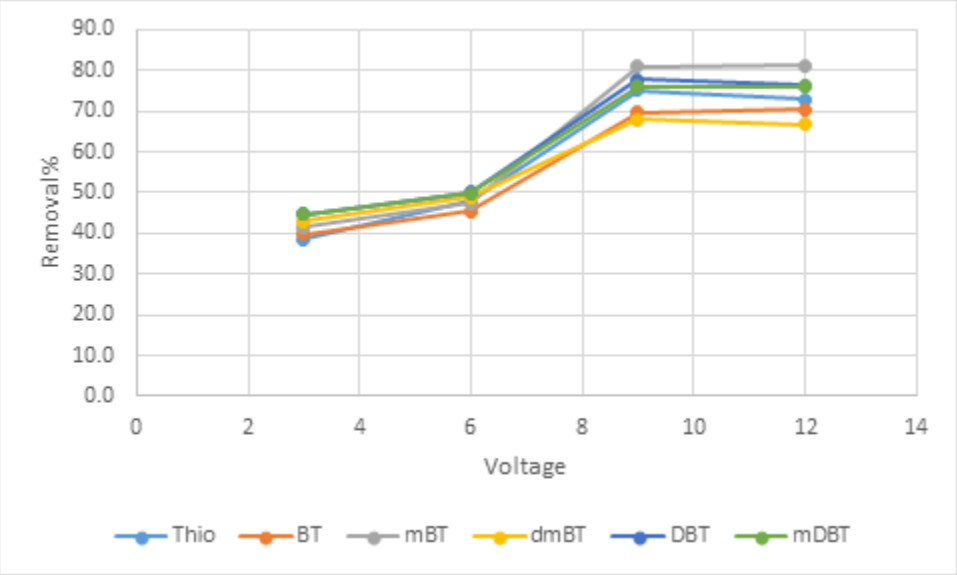


Figure 26: Optimization of the speed of the reactor motor

4.2.1.3 Optimization of pumps combined flow rate

Different flow rates for the pump were applied 5, 10, 20 and 40 ml/min and 9V for the reactor voltage and 100 µm for the reactor gap size and as it clear in the graph after flow rate 10 ml/min the removal efficiency decreases, that's because the residence time of the sample is time independent, and depend on the flow rate of the sample by the pumps, so by increasing the flow rate more than 10ml/min the sample residence in the reactor is dramatically decreased and the mixing efficiency also decreases and that's why the removal decreases, so 10 ml/min was selected to be the optimum parameter.

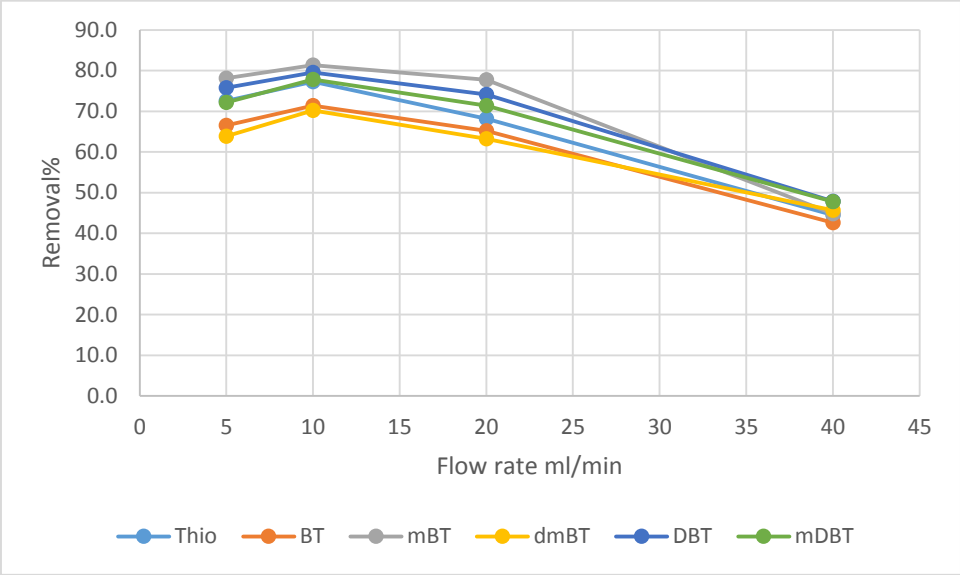


Figure 27: Optimization of pumps combined flow rate

4.2.1.4 Optimization of the Gap Size

The gap size of the reactor was optimized, different gaps were investigated 100, 200, 300 and 500 µm from the graph the optimum gap was 100 µm and by increasing the gap size the removal efficiency decreases, that can be attributed by the small gap give the highest surface area for the reaction and the highest removal efficiency.

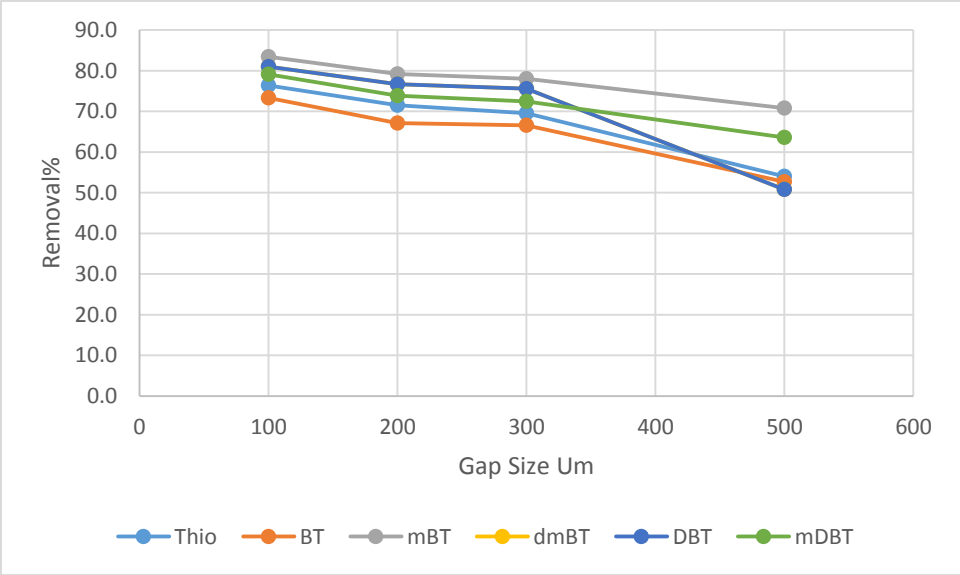
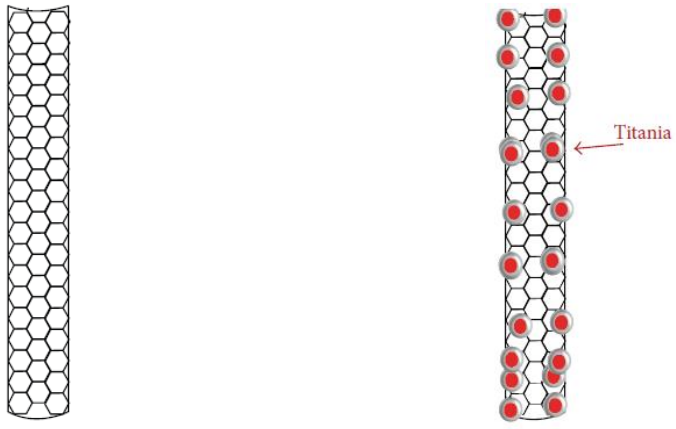


Figure 28: Optimization of the Reactor Gap size

4.2.2 Comparison between TiO_2, CNT & CNT/ TiO_2 composite

Nanocomposite of CNT/TiO_2 showed a better desulfurization activity than TiO_2 alone, Addition of CNT to Titania enhanced the removal, that's due to the high surface area and porosity of the CNT which provide more active site, also CNT prevent the Titania from agglomeration which reduce the activity of the sorbent.



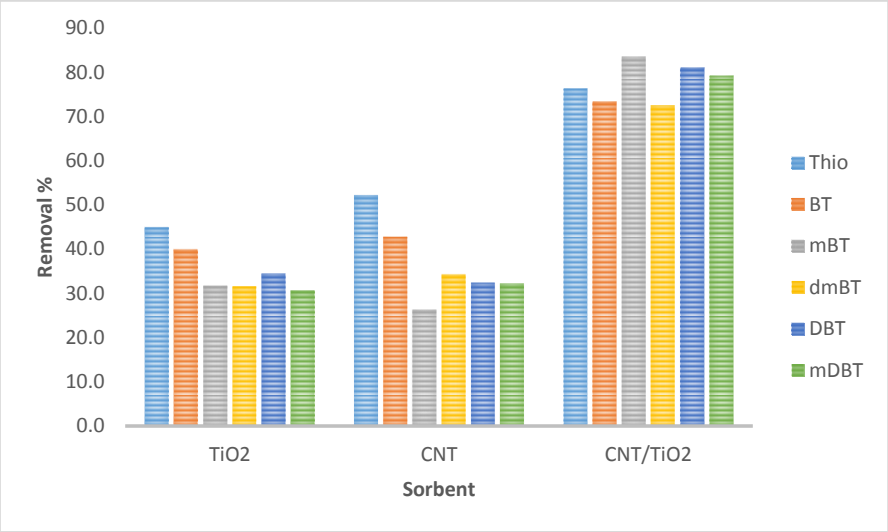


Figure 29: A comparison between the desulfurization activity of CNT, titania, and the prepared CNT/TiO_2

The proposed mechanism for the removal using the composite is acid base interaction, because the sulfur atom contain lone pair of electron and the titanium atom contain empty orbital so the sulfur act as Lewis base and the titanium act as Lewis base.

So the EDX experiment was carried out before and after the adsorption and there's obvious change in the morphology of the composite surface.

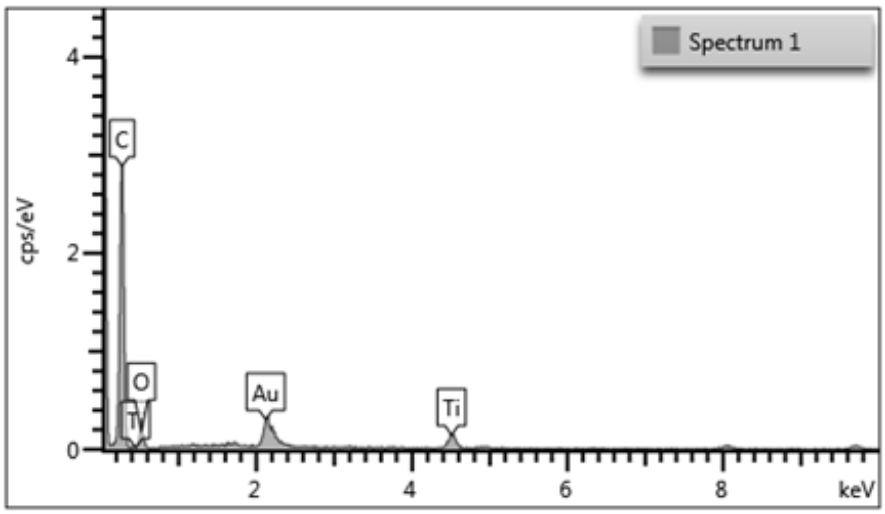


Figure 30: EDX for the composite before adsorption

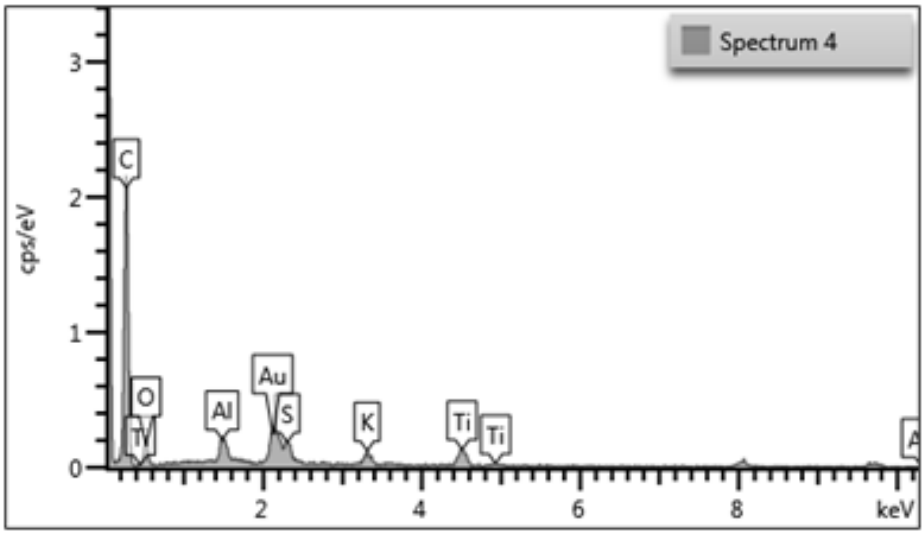


Figure 31: EDX for the composite before adsorption

The IR experiment was done to conform the mechanism of the removal, a small shift was observed in the titanium oxygen bond from 834 to 750 cm^{-1} and that indicate the interaction of sulfur atom to the titanium.

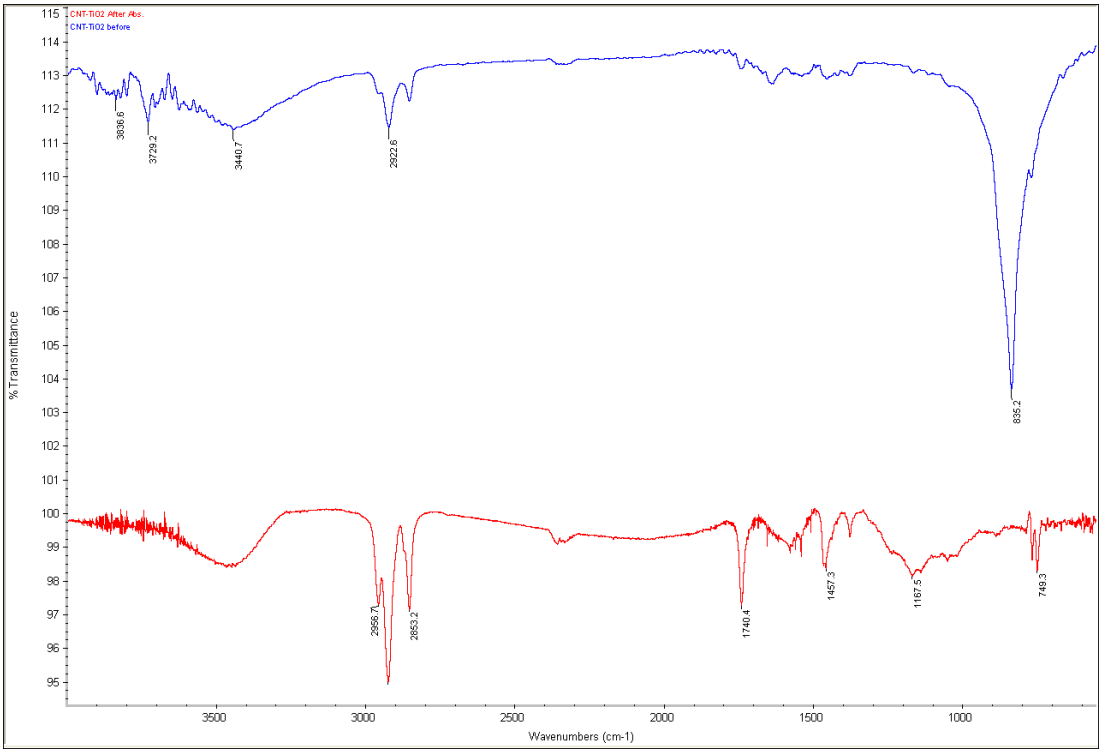


Figure 32: FT-IR before & after the adsorption

4.2.3 Regeneration of CNT/ TiO_2

After the first run for the CNT/ TiO_2 composite for the removal of sulfur compound from crude oil model the composite was collected and placed in the oven at 400C for 3h, after it was cooled down the composite was reused for another two cycle and the results showed that the nanocomposite is regenerated.

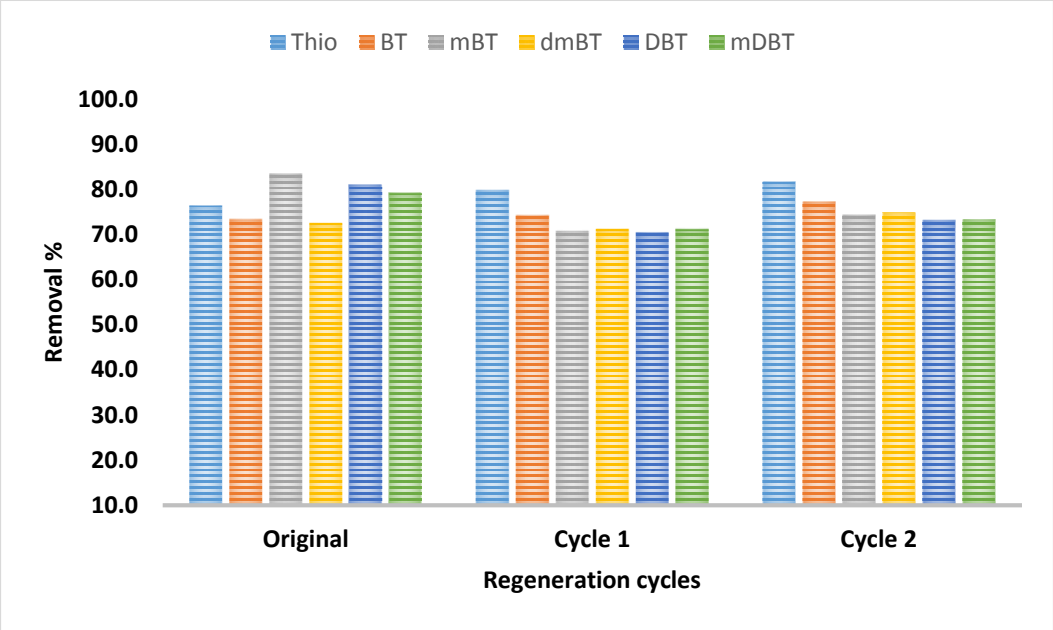


Figure 33: Regeneration cycles of CNT/TiO_2

4.3. Film shear reactor combined with membrane reactor

As it expected the combination of the film shear reactor and membrane reactor enhanced the removal of sulfur compounds from the crude oil model sample and as we can see in the figure below the combination of the two reactors gave a very good results.

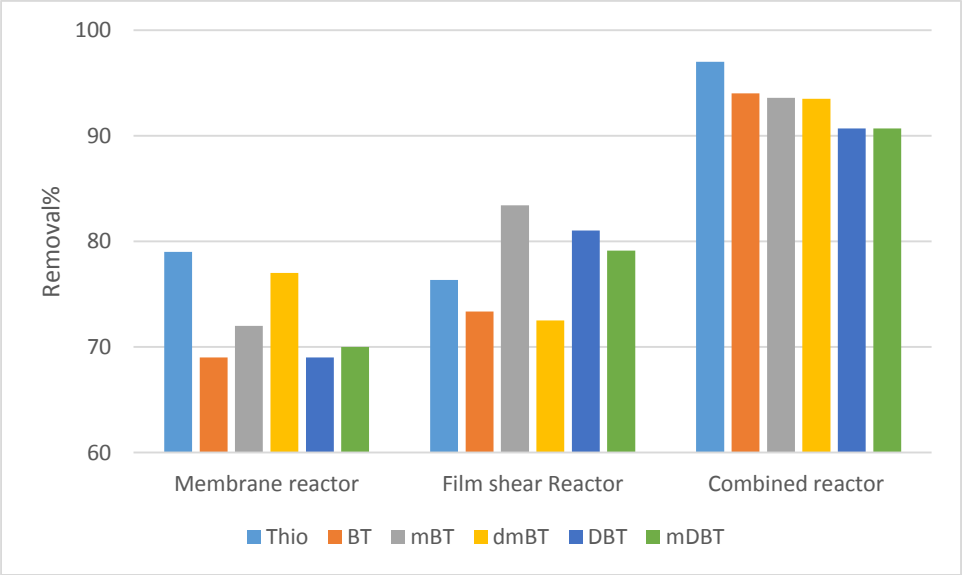


Figure 34: Comparison between membrane reactor, film shear reactor and the combined reactor.

CHAPETR 5
CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

For the first time the electro-coated membrane flow reactor was used for the removal of sulfur contaminants in diesel samples, the proposed method is simple, fast, inexpensive and efficient, the parameters of the removal were optimized and the removal efficiency was around 79%, and also the removal kinetic was investigated and was fitted to the pseudo second order.

Another method was investigated for the removal of sulfur compounds form the crude oil, that's methods is film shear reactor, in that methods the a suspension of composite of titania and carbon nanotube was used in, that composite was prepared and characterized with different characterization methods and the parameters of the reactor was optimized that method is simple, very fast and the reactor showed high removal efficiency about 80% for the sulfur compounds.

Lastly the film shear reactor was combined with membrane reactor and that combination showed high removal efficiency near to 100%

5.2. Recommendations

Recommendation I

Try to investigate more different membranes for the removal of sulfur compounds in the crude oil.

Recommendation II

Investigate different nanoparticles and composites for the coating of membrane for the removal of sulfur compounds in the crude oil or for other applications.

Recommendation III

Investigate the use of other nanocomposite instead off the CNT/TiO_2 in film shear reactor for the removal of sulfur compounds in the crude oil or for other applications.

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Vitae

Name	:Munzir Hamedelniel Mohamed Suliman
Nationality	:Sudanese
Date of Birth	:7/5/1989

Email	:g201304270@kfupm.edu.sa
Address	:KFUPM/Student housing Building 804 Room 210

Academic Background	B. Sc. in chemistry in Sudan University for Science and Technology
Work Experiences	December 2011 - December 2012 Lab teaching assistant, Chemistry Dept. Sudan University of science and technology. March 2012 – July 2013 QC Analyst, Tabuk Pharmaceutical CO. Khartoum north, Sudan
Publications	Ibrahim Al-Zahrani, **Munzir H. A. Mohammed**, Chanbasha Basheer, Mohammad Nahid Siddiqui, and Abdulrahman Al-Arfaj: "Membrane Assisted Simultaneous Extraction and Derivatization with Triphenylphosphine of Elemental Sulfur in Arabian Crude Samples by Gas Chromatography/Mass Spectrometry", *Journal of Chemistry,* **January 2015**, Article ID 792914. (Published) **Munzir H. A. Mohammed**, Chanbasha Basheer, Mohammad Nahid Siddiqui, Salawu Omobayo Adio and Ismailia Y. Abdulkareem: "Desulfurization of Fuel Oil using Silver Nanoparticles Coated Electro-Membrane Flow Reactor Journal of Industrial and Engineering Chemistry",

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